DISSOLUTION OF OLIVINE, SIDERITE, AND BASALT AT 80°C IN 0.1 M H_2SO_4 IN A FLOW THROUGH PROCESS: INSIGHTS INTO ACIDIC WEATHERING ON MARS.

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Introduction: The occurrence of jarosite, other sulfates (e.g., Mg-and Ca-sulfates), and hematite along with siliciclastic materials in outcrops of sedimentary materials at Meridiani Planum (MP) and detection of silica rich deposits in Gusev crater, Mars, are strong indicators of local acidic aqueous processes [1,2,3,4,5]. The formation of sediments at Meridiani Planum may have involved the evaporation of fluids derived from acid weathering of Martian basalts and subsequent diagenesis [6,7]. Also, our previous work on acid weathering of basaltic materials in a closed hydrothermal system was focused on the mineralogy of the acid weathering products including the formation of jarosite and gray hematite spherules [8,9,10]. The object of this research is to extend our earlier qualitative work on acidic weathering of rocks to determine acidic dissolution rates of Mars analog basaltic materials at 80°C using a flow-thru reactor. We also characterized residual phases, including poorly crystalline or amorphous phases and precipitates, that remained after the treatments of olivine, siderite, and basalt which represent likely MP source rocks. This study is a stepping stone for a future simulation of the formation of MP rocks under a range of T and P.

Experimental: San Carlos forsterite (SCO) and hand specimens of Londonderry, Nova Scotia, siderite (SL) were obtained from Wards Natural Science [10]. Clean mineral grains were hand-picked and ground with an agate mortar and pestle under acetone. The ground samples were separated into 50-5 μm by sieving and gravity sedimentation. A basaltic rock (OB) from Kona, Hawaii, was ground and separated into 50-5 μm fraction in a similar fashion. Specific surface areas were determined by a BET-N_2 adsorption method using a Micromeritics Gas Adsorption apparatus.

Flow-through experiments: A 2-g sample of the mineral/rock was placed in a Parr flow through hydrothermal reactor, where all the parts in contact with liquid were acid resistant PEEK or Ti metal. The flow rate was maintained at 0.1 ml/min using a metering pump and the packed mineral column was retained at both ends by Teflon frits to prevent any particle loss. The leaching experiments were run at 80°C for 10-12 days, and the solution samples were collected for 24-h intervals except in the first two days where samples were collected more frequently. The acid leachates were analyzed for pH, Mg, Fe, Ca, Na, K, and Mn using a Fisher Accumet pH meter and Perkin Elmer, AAnalyst 800, Atomic Absorption Spectrometer with AS 800 Autosampler. Column residue was freeze-dried for further analyses by SEM, EDS and XRD. The solution data were fitted to a disappearing sphere model [11,12] to obtain the forward dissolution rates of the particles with changing surface area.

Composition: The San Carlos forsterite was free of mineral impurities, whereas the Londonderry siderite was mainly Fe-Mg-zoned magnesio-siderite with minor ankerite

inclusions. Basalt from Kona, Hawaii contained pyxroxene, plagioclase and ferroan forsterite as major components.

Mineralogy of the end products: SCO dissolved leaving amorphous silica and unreacted olivine residue (Figures 1a and 1b), the siderite dissolved leaving no recognizable mineral residue, and the basalt dissolved incongruently, with olivine dissolving completely and plagioclase and pyroxene and other phases dissolving partially leaving a residue rich in pyroxene (1c) and Ti (1d). Olivine dissolution released SiO_4^{4-} into solution which resulted in precipitation of a SiO_2 cast around the original olivine particle (See Figure 1a). In SCO residue, small Mg- and Fe-rich particles were present in addition to the voids made of silica casts (not shown). Silica casts of dissolved olivine and precipitated Si throughout the matrix were observed in residue from acid-treated Kona basalt (Figure 1c). Ti, Mg, Al, Ca and some Fe were observed in the solid residue containing residual pyroxene (only Ti shown in Figure 1d).

Leachate chemistry: The olivine solubility was calculated from Mg data (stoichiometry = 1.8). Because the dissolution rate at acid pH did not reach steady state as has been reported previously for very acidic solutions [11,12], the disappearing sphere model of Lasaga [11] was used to calculate the dissolution rate (Table 1).
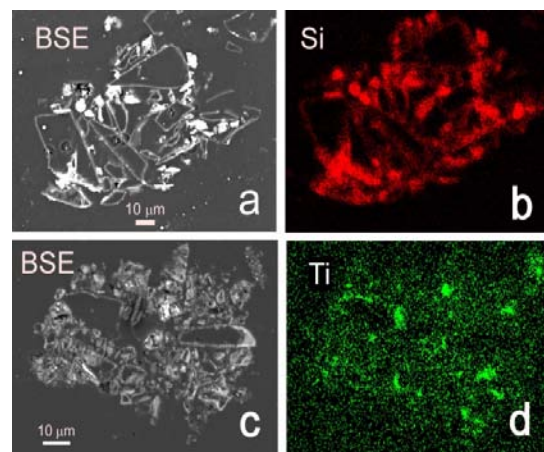
Figure 1. Backscatter image of sectioned epoxy embedded acid leached simulants: (a) SCO showing crystal molds of olivine, (b) silica residue from leached SCO, (c) Kona basalt showing similar molds to (a), and (d) leached basalt residue rich in Ti.

The solution chemistry data for SCO indicated that Fe/Mg ratio remained constant and similar to that in the parent mineral, indicating congruent dissolution with respect to these two cations [e.g., 13 and references therein]. In the case of Londonderry siderite, a similar congruent dissolution was observed. However, the filtered initial samples collected at high pH caused some precipitation of ferric hydroxide, which was arrested by adding sufficient concentrated HCl. The dissolution rates of SCO and SL fitted well

with the disappearing sphere model (Figure 2) and were similar to literature data (Table 1).
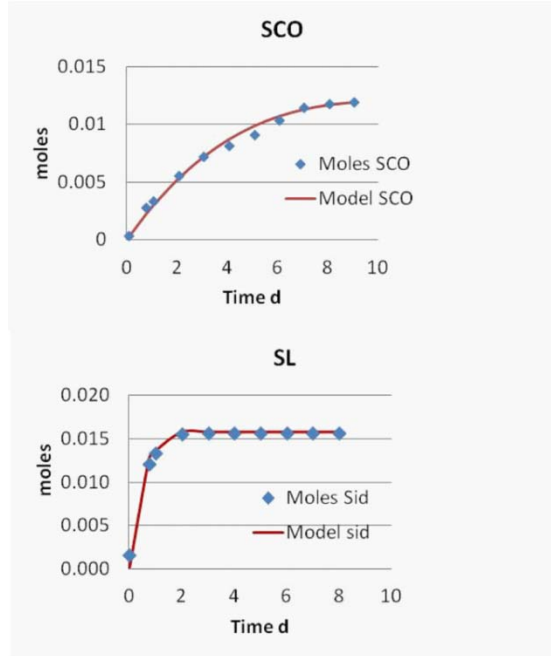

Figure 2. Model fits for cumulative dissolution of San Carlos olivine (SCO) and siderite (SL) vs. time (days).

Table 1: Dissolution rates of individual minerals and basalt.

Mineral	R_0 (m)	K $(mol.cm^{-2}.sec^{-1})$	pH
Minerals			
Forsterite (SCO)	$7.8x10^{-6}$	$1.76x10^{-11}$	1.19
Siderite (SL)	$7.0x10^{-6}$	$2.05x10^{-10}$	1.79
basalt (OB)			
olivine	$8.2x10^{-6}$	$1.10x10^{-10}$	1.21
* M1	$8.2x10^{-6}$	$5.80x10^{-12}$	1.21
* M2	$8.2x10^{-6}$	$4.30x10^{-13}$	1.21
* M1 and M2 are two Ca bearing phases of different dissolution rates in OB, which may represent a plagioclase and a pyroxene (R_0 = geometric particle radius in meters).			

The dissolution rate of forsteritic olivine in OB based on Mg data is slightly greater than that of SCO. This increase may be attributed to compositional differences (increased Fe) or result from Mg coming from sources other than olivine. Dissolution of plagioclase and pyroxene in basalt was followed using Ca release rates by assuming two Ca bearing minerals of differing dissolution rates (rate M1 > rate M2) and the data are shown in Table 1 and Figure 3. Their rates of dissolution are reasonable matches for pyroxene and plagioclase cosidering compositional variability [14,15] and account for the total Ca released (Figure 3). However, whether these two mineral phases uniquely represent plagioclase and pyroxene need to be further ex-

amined. A similar approach was used to resolve Mg-dissolution rates of olivine and pyroxene in OB (not shown).

Conclusions: Dissolution of forsterite has been studied extensively, and the purpose of this study was to study forsterite, siderite and basalt in the context of Martian rock formation under acidic conditions. Silica cast formation of olivine in flow-thru experiments were similar to that observed in previous batch type and flow through experiments [e.g., 16]. A sulfuric acid reacted SCO in a closed vessel, after evaporation contained similar crystal molds (unpublished data). Dissolution data presented here provides insights into the acid dissolution rates of pure minerals and rocks in a flow-thru situation similar to MP (pH = 1-2) where acids may have upwelled through the sediments (e.g., 7). Removal of the soluble cations leaves behind a mostly silica rich residue with few mineral remnants [e.g., 5]. However the incorporation of the leachate as an evaporite into the leached rock (low water to rock ratios) may mimic isochemical weathering. The presence of silica casts in rapidly dissolving olivine in acidic media may offer another explanation to the crystal molds observed in Meridiani evaporitic rocks. Completion of previous batch experiments [10] and the current flow-through experiments set the stage for a final experiment to test whether isochemical acidic weathering of rocks (i.e., evaporation of combined leacheate and residue) under oxidizing conditions at elevated T and P produce MP-like rocks using a Parr flow-thru hydrothermal reactor.
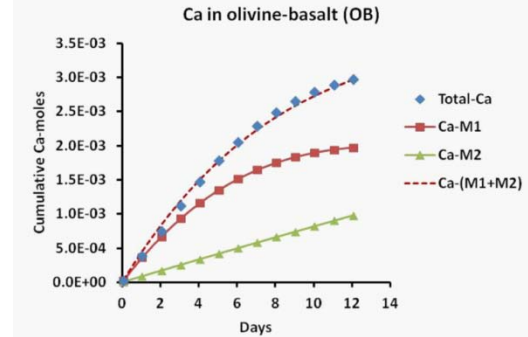
Figure 3. Model fits for total Ca released from basalt by assuming 2 Ca-releasing minerals M1 and M2 of differing solubility in OB (e.g., plagioclase and pyroxene).

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